

Cu_xS back contact for CdTe solar cells

Donghwan Kim*, B.E. McCandless, S.S. Hegedus, and R.W. Birkmire
*Institute of Energy Conversion, University of Delaware,
 Newark, Delaware 19716, U.S.A.*

Recibido el 9 de junio de 2006; aceptado el 26 de octubre de 2006

Copper sulfide (Cu_xS) films were studied as a back contact material for CdTe solar cells. The Cu_xS films were made by chemical bath deposition in aqueous solution. Annealing at 200°C in Ar improved the performance of the solar cells. Using the CdS/CdTe/Cu_xS/C structure, an open-circuit voltage (V_{oc}) higher than 840 mV and an energy conversion efficiency higher than 11% were obtained.

Keywords: Copper sulfide; cadmium telluride; solar cells; contact resistance.

Se estudiaron películas de sulfuro de cobre (Cu_xS) como material de contacto posterior para células solares de CdTe. Las películas de Cu_xS se hicieron por deposición en baño químico de solución acuosa. El recocido a 200°C en Ar mejoró el rendimiento de las células solares. Mediante la estructura CdS/CdTe/Cu_xS/C, se obtuvo un voltaje de circuito abierto (VCA) superior a los 840 mV y una eficacia de conversión de energía superior al 11%.

Descriptores: Sulfuro de cobre; telurio de cadmio; celdas solares; resistencia de contacto.

PACS: 84.60.Jt; 73.40.Cg

1. Introduction

CdTe is one of the most promising materials for thin-film solar cells along with thin-film Si and CuInGaSe₂. High-efficiency CdTe solar cells can be fabricated by a wide variety of methods and the technology is on the verge of a large-scale commercialization [1].

The highest energy conversion efficiency for a CdTe cell is about 16% for an area of 1 cm² [2]. However, efficiencies of large-area modules (typically 60 × 90 cm²) are around 8%. The high series resistance (R_s) is one of the reasons for the large difference in performance between the small-area cells and the large-area modules. The major source of R_s is the high contact resistance between CdTe and the back contact.

Forming an ideal ohmic contact to CdTe is difficult because the work function of p-type CdTe is higher than most metals. Two approaches have been studied to reduce the contact resistance, namely, (1) doping the CdTe surface at a high level, or (2) placing a buffer layer between CdTe and the electrode. The buffer layer must have a high electrical conductivity and a good band alignment with CdTe as well. In many cases the distinction between the two approaches is not clear because the buffer layer can be the source of the dopant impurities for CdTe. Excellent reviews on this topic were given by Fahrenbruch [3] and Dobson *et al.* [4].

Cu_xS seems to have properties suitable for a buffer layer. For example, the chalcocite phase (Cu_{1.96}S) has the same electron affinity as CdTe and the bandgap of 1.2 eV [5]. The energy barrier between CdTe and Cu_xS is expected to be small. Cu_xS also has a high electrical conductivity [5].

Cu_xS was actively studied until the early 1980s as the first all-thin-film solar cell material. An excellent summary on Cu_xS solar cells was made by Fahrenbruch and Bube [5]. The performance of Cu_xS solar cells degraded with time due to the diffusion of Cu in the electric field. The degradation of

Cu_xS solar cells discouraged further research and development efforts. However, as a back contact material, Cu_xS may be stable because it is not positioned in a strong electric field, though there may be a weak field due to the contact with the highly resistive CdTe.

Various methods were used for the fabrication of Cu_xS [6]. In this study, we used the chemical bath deposition (CBD) in order to keep the processing temperature low for minimizing the Cu diffusion into CdTe during deposition. To the best of our knowledge, this is the first work on applying Cu_xS to CdTe solar cells.

2. Experimental procedures

Substrates of glass/SnO₂/CdS/CdTe were obtained from a commercial source [6]. Substrates of size 1"×1" were etched in a 0.01% bromine-methanol solution for five seconds to prepare the CdTe back surface for contacting.

Cu_xS films were deposited by CBD as reported by Fatas *et al.* [7]. An aqueous solution of 0.1 M copper sulfate, 0.1 M sodium acetate, 0.37 M triethanolamine, and 0.03 M thiourea was used. The pH of the solution was adjusted to 9.4 with ammonia solution. The deposition was carried out at 40°C for 15 minutes. The samples were annealed at 200°C in Ar atmosphere for different lengths of time. Carbon (Acheson 505SS carbon ink) contacts were applied and were cured at 100°C in air for five minutes after drying at room temperature. Current-voltage (J-V) measurements were done both in the dark and under illumination. Energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD) were performed on Cu_xS.

3. Results and discussions

Figure 1 shows the results of the light current-voltage (J-V) measurement on the CdTe samples with Cu_xS. The performance of the cells improved as the annealing time increased up to 80 min at 200°C. Similar data were reported by Gessert

et al. [8], in which both the open-circuit voltage (V_{oc}) and the fill-factor (FF) increased with the thickness of ZnTe buffer layer doped with Cu. Gessert *et al.* explained that the diffusion of Cu from ZnTe into CdTe made CdTe more conducting and thus increased both the V_{oc} and the FF of the cell. Similar trends were reported by Pudov *et al.* [9]. They reported that the FF increased with the thickness of “Cu-containing layer” in the CdS/CdTe/“Cu-layer”/C structure. The same argument can be used to explain the results shown in Fig. 1, *i.e.*, diffusion of Cu from Cu_xS into CdTe during the heat treatment. As the annealing time increased, more Cu moved to CdTe and thus increased the V_{oc} and the FF.

Loss of Cu in Cu_xS may lead to the decrease of electrical conductivity in Cu_xS and thus to a change in the characteristics of the CdTe/ Cu_xS junction. Figure 2 shows the results of current-voltage measurements in the dark plotted as dV/dJ vs. $1/J$ [10]. The curvature at high currents (low $1/J$) is indicative of a blocking contact. The results show that the “roll-over” in the dark J-V curve became larger as the annealing time increased.

A possible explanation is that Cu moved out of Cu_xS during the annealing and made Cu_xS less electrically conducting which in turn made the characteristics of the CdTe/ Cu_xS junction closer to that of a blocking contact. Changes in the characteristics of the back contact as a result of Cu diffusion is a commonly observed phenomenon when Cu is used in the back contact of CdTe [11]. The “roll-over” in the dark J-V curve becomes significantly smaller under illumination as shown in Fig. 1 due to the photoconductivity effect in Cu_xS .

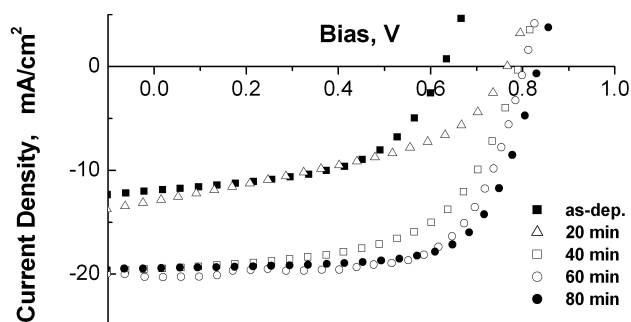


FIGURE 1. Light current-voltage results of CdTe cells with Cu_xS back contacts.

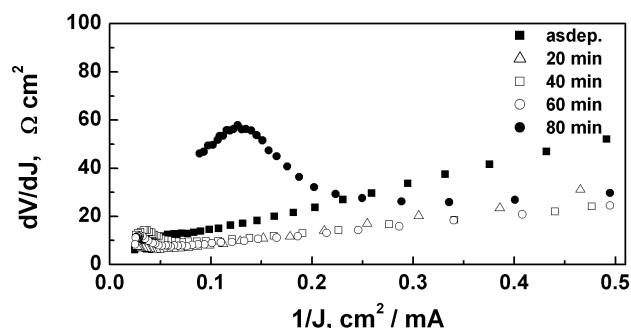


FIGURE 2. Change of dark current-voltage characteristics in CdTe cells annealed over different time durations.

A different view to explain the results in Fig. 1 is also possible. The copper that was already present in CdTe became electrically active after annealing. During the Cu_xS deposition, Cu ions in the aqueous solution may infiltrate into the CdTe through grain boundaries. It is also possible that the Cu may reach the CdS/CdTe interface. Supporting evidence for Cu diffusion into CdTe during the Cu_xS deposition is the fact that the cells were completely shorted when a complexing agent such as triethanolamine (TEA) was not used to keep the Cu ions at a low concentration in the aqueous solution [12]. Other evidence for the Cu presence in CdTe is that the cells with as-deposited Cu_xS not only showed a lower photovoltaic performance but also showed a bias dependence of the photocurrent under the reverse bias (Fig. 1).

The bias dependence of the photocurrent may be shown more clearly by quantum efficiency (QE) measurements as given in Fig. 3. Figure 3 shows that QE increases under reverse bias and decreases under light bias. The difference between the non-biased and the biased became smaller with annealing. For the sample with 60 min. annealing, the difference became negligible.

It should be noted that the shape of the QE curves did not change under bias. Mitchell *et al.* [13] suggested that when the interface recombination is the dominant loss mechanism of the photogenerated carriers, the shape of the QE curves do not change with bias. The results in Fig. 3 suggest that Cu diffused to CdS/CdTe junction during the Cu_xS deposition and created recombination centers which disappeared after the heat treatments. At the same time, it is also possible that the Cu in grain boundaries became electrically active after the annealing and contributed to the increase in V_{oc} and FF.

The change of the cell performance with the annealing time is summarized in Fig. 4. Both V_{oc} and FF saturated beyond the annealing time of 80 min, but J_{sc} decreased with further annealing, probably because of excess Cu diffusion into CdTe. In order to clarify the issue of Cu diffusion, depth profiling should be performed.

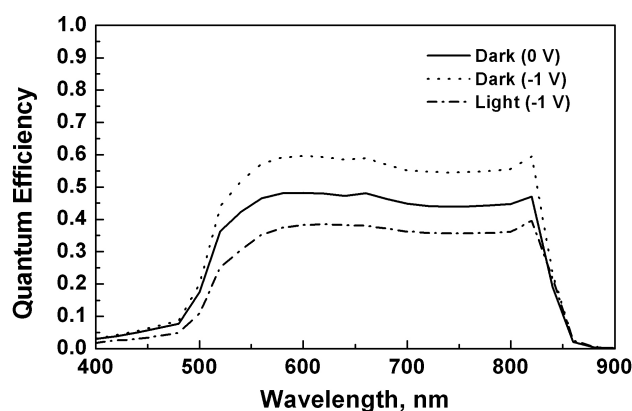


FIGURE 3. Spectral response curves at different bias conditions for a CdTe cell with an as-deposited Cu_xS layer.

TABLE I. Change in composition and electrical properties of Cu_xS film on slide glass before and after annealing.

Annealing Time	Cu/S Ratio	Carrier Density [cm ⁻³]	μ [cm ² / V · s]	ρ [Ω cm]	Rs [Ωvsq]
None	0.88	1.13 × 10 ²¹	3.08	2.03 × 10 ⁻³	406
60 min.	1.1	1.58 × 10 ²²	1.78	2.33 × 10 ⁻⁴	47

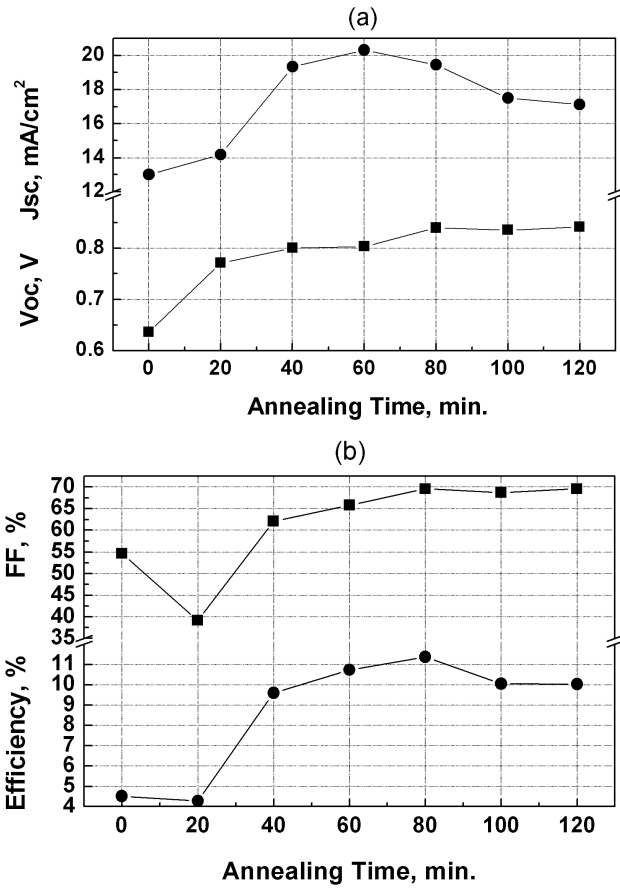


FIGURE 4. Summary of light J-V measurements on CdTe cells with different annealing time after Cu_xS deposition. (a) V_{oc} and J_{sc} vs. annealing time and (b) FF and efficiency vs. annealing time.

Cu_xS undergoes a dramatic change during annealing. As-deposited Cu_xS has an amorphous phase as shown in the x-ray diffraction (XRD) pattern in Fig. 5. After annealing at 200°C for one hour in Ar atmosphere, three peaks appeared that matched with the covellite phase (CuS). The XRD results coincide well with the chemical analysis of the sample by energy dispersive x-ray spectroscopy (EDS) in which Cu/S ratios close to 1 are shown (Table I). The XRD results can be compared with the report by Nair *et al.* [14]. However, Nair *et al.* studied films with Cu/S = 1 and did not find a compositional change in their CuS after annealing at 200°C. The sample used in this study did not have the stoichiometric composition (Cu/S = 1) before annealing and thus probably contained free sulfur which evaporated during annealing.

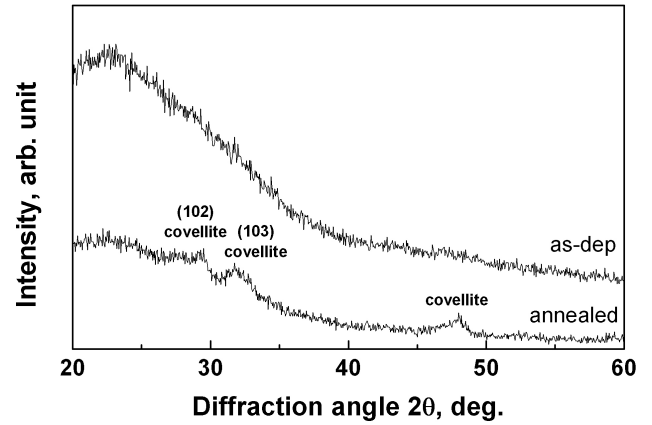


FIGURE 5. X-ray diffraction patterns of Cu_xS on glass substrates before and after annealing at 200°C for 1 hr in Ar. The film was about 50 nm in thickness.

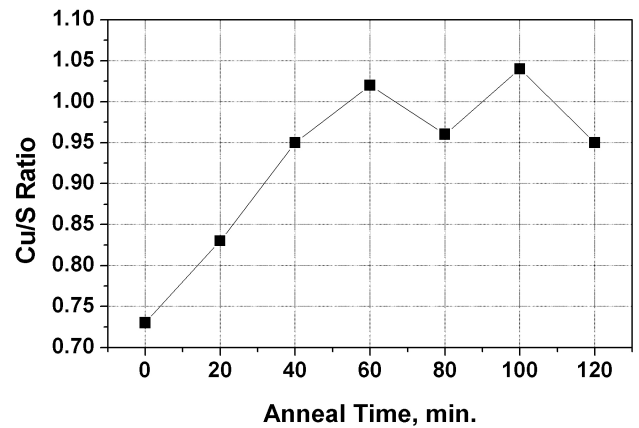


FIGURE 6. Change of Cu/S ratios in Cu_xS films after annealing. Cu_xS films were coated on CdTe substrates.

Cu_xS films became more electrically conducting as shown in Table I, probably as a result of the crystallization. The contribution of the compositional variation to the change of the electrical properties needs to be studied.

The composition of Cu_xS changed as a result of the heat treatment at 200°C in Ar atmosphere (Fig. 6). The films became Cu-rich after annealing. The fluctuation in the Cu/S ratio for longer annealing times is believed to be due to experimental error. The data in Fig. 6 do not necessarily contradict the earlier argument that Cu diffuses out of Cu_xS into CdTe because the probing depth of EDS measurement is on the order of a micron.

4. Summary

Cu_xS films were made by chemical bath deposition and were applied to CdTe solar cells as the back contact material. The performance of the cells showed a large improvement after annealing at 200°C in Ar. Using the CdS/CdTe/Cu_xS/C structure, the highest performance obtained from this work was $V_{oc}=840$ mV, $J_{sc} = 19.45$ mA/cm², FF = 69.6%, and efficiency = 11.37%, which was comparable to results obtained with other more mature contact processing. With further op-

timization, Cu_xS could be a viable contact for high-efficiency CdTe solar cells.

Acknowledgments

The authors wish to thank First Solar, Inc. for the CdTe samples. One of the authors (Donghwan Kim) was partially supported by the Korea Ministry of Commerce, Industry and Energy through the academic promotion program of the Korea Energy Management Corporation (KEMCO).

* On leave from Korea University, Seoul, Korea.

1. A. Goetzberger and C. Hebling, *Solar Energy Materials and Solar Cells* **62** (2000) 1.
2. N. Romeo, A. Bosio, R. Tedeschi, and V. Canevari, *Materials Chemistry and Physics* **66** (2000) 201.
3. A.L. Fahrenbruch, *Solar Cells* **21** (1986) 299.
4. K.D. Dobson, I. Vily-Fisher, G. Hodes, and D. Cahen, *Solar Energy Materials and Solar Cells* **62** (2000) 295.
5. A.L. Fahrenbruch and R.H. Bube, *Fundamentals of Solar Cells* (Academic Press, New York, 1983) p. 417.
6. D. Rose *et al.*, Proc. 28th IEEE Photovoltaic Specialists Conference (2000) 428.
7. E. Fatas *et al.*, *Materials Chemistry and Physics* **12** (1985) 121.
8. T.A. Gessert, M.J. Romero, S. Johnston, B. Keyes, and P. Dippo, Proc. 29th IEEE Photovoltaic Specialists Conference (2002) 536.
9. A.O. Pudov *et al.*, Proc. 29th IEEE Photovoltaic Specialists Conference (2002) 760.
10. S.S. Hegedus, B.E. McCandless, and R.W. Birkmire, Proc. 28th IEEE Photovoltaic Specialists Conference (2000) 535.
11. S.E. Asher *et al.*, Proc. 28th IEEE Photovoltaic Specialists Conference (2000) 479.
12. I. Grozdanov and M. Najdoski, *J. Solid State Chem.* **114** (1995) 469.
13. K.W. Mitchell, A.L. Fahrenbruch, and R.H. Bube, *J. Appl. Phys.* **48** (1977) 4365.
14. M.T.S. Nair, L. Guerrero, and P.K. Nair, *Semiconductor Science and Technology* **13** (1998) 1164.